

Black Silicon Anti-Reflection: Increased Wafer Silicon Efficiency with Reduced Manufacturing Costs

Program Team: PV

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Timeline

- Project start date: Feb. 01, 2010
- Project end date: Jan. 31, 2012
- Percent complete: 12%

Budget

- Total project funding
 - DOE: \$1M
- Funding received in FY10: \$333k
- Funding for FY11: \$500k

Barriers

- Poor broad-spectrum and off-angle anti-reflection (AR) performance in Si PV
- Costly vacuum-based interference AR coatings
- Toxic and greenhouse gases

Partners

- Project lead: NREL
- Interactions/collaborations:
 - 6 crystalline-Si PV companies, 2 chemical companies
 - 2 start-up companies

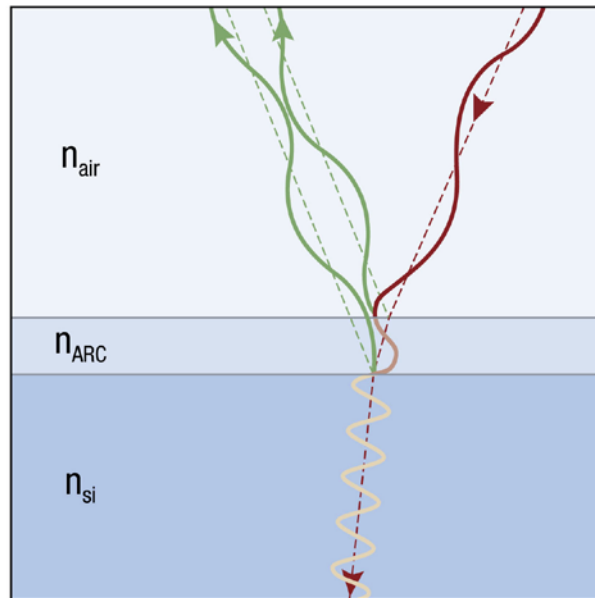
- Conventional interference-based AR on crystalline-Si
 - Reflection losses 3-10% across spectrum
 - Poor angular acceptance of incident photons
 - Costly vacuum-based deposition (normally SiN_x)
 - Mostly PECVD
 - hazardous process gases
 - greenhouse-gas cleaning gases
 - Some sputtering
- NREL one-step, liquid black Si etch
 - Excellent AR over broad spectrum
 - potential to improve solar energy conversion efficiency
 - Improved angular acceptance for high annual energy production
 - Inexpensive liquid bath texture etch

Conventional Anti-Reflection Combines Coating and Texture

Multicrystal Si: ~7% reflection loss

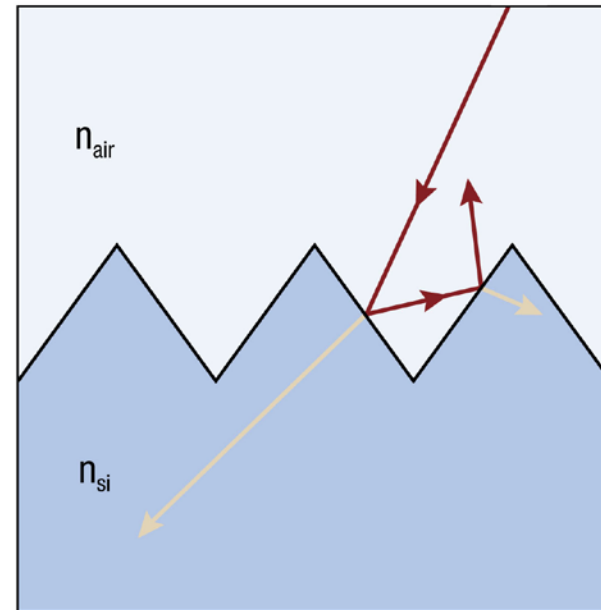
Single crystal Si: ~ 3% reflection loss

Antireflection coating



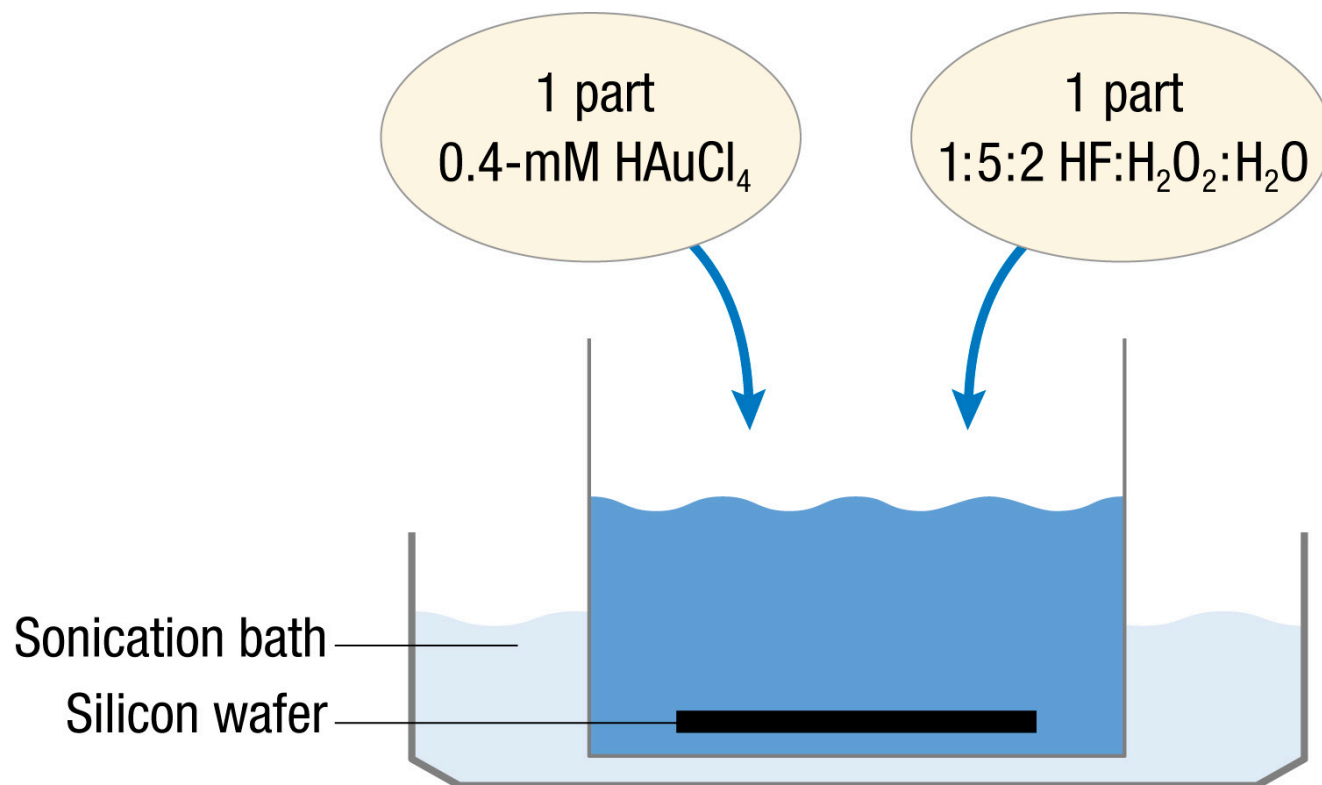
- Interference anti-reflection coating
- Suppress reflection at one fixed wavelength
- Requires vacuum-based deposition tools

Textured surface



- Multiple reflections broaden spectrum
- μm -scale surface texture
- Broad-band AR only at *near normal* angles

Background: NREL's One-Step, All-Liquid Black Si Etch



- Excellent AR after 3-min etch at room temperature, <1 min at 40°C

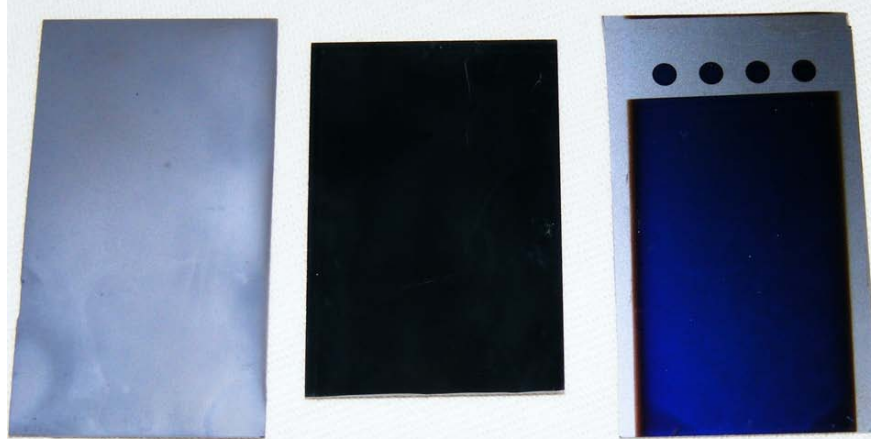
Background: Appearance of Black Si

μm -scale textured
mono-Si

3-min
black Si

μm -scale textured +
anti-reflection coating

Near normal angle:



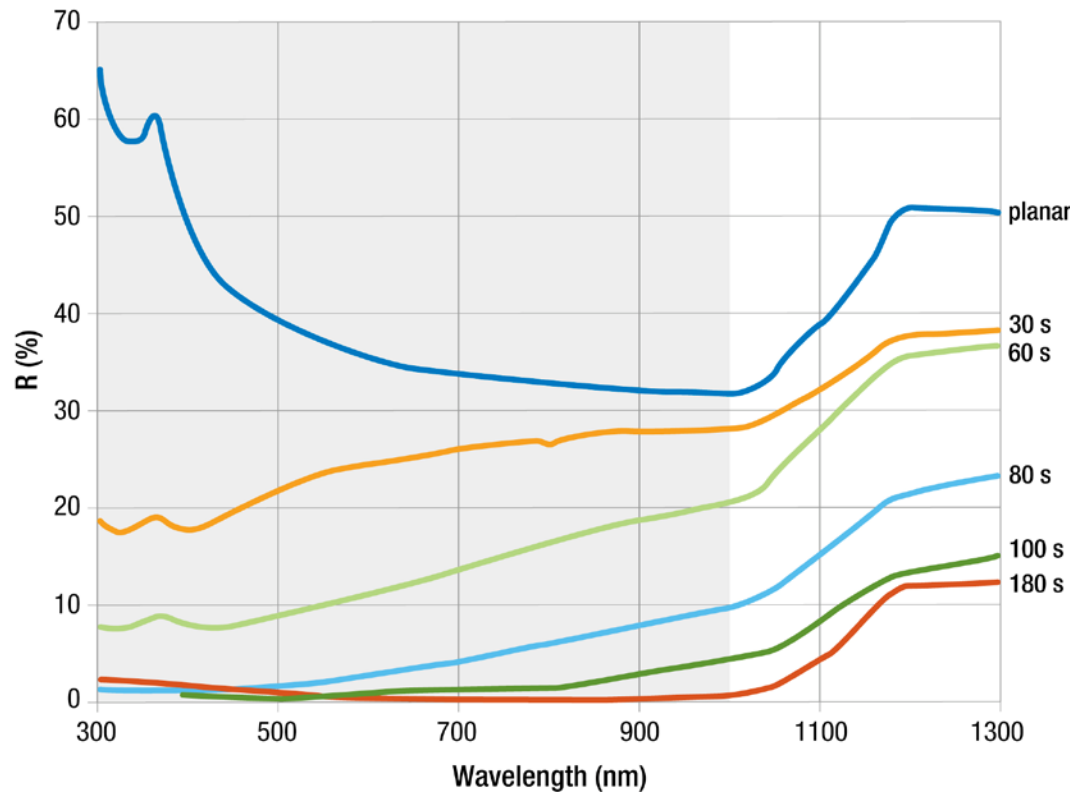
Tilted angle:



- Conventional AR scheme has low reflection at near normal angle but high reflection at titled angle
- Black Si surface remains dark at various angles

Background: Black Si Reflectance below 2% for entire spectrum

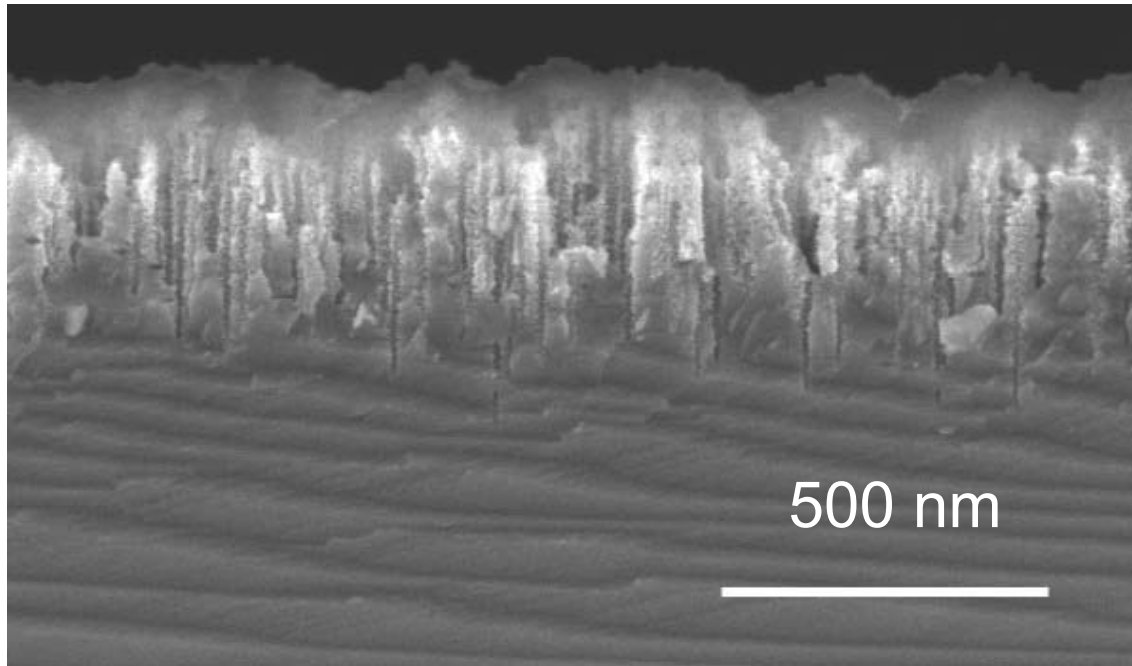
Branz et al. APL, 2009



- Reflection suppression starts at short wavelength and progresses to long wavelength as black Si etch time increases

Background: SEM Image of 3-Min Black Si

Branz et al. APL, 2009



- Nano-porous surface layer
- 3-min black Si etch at room temperature produces pores in diameter of ~ 10 nm and depth of ~ 600 nm

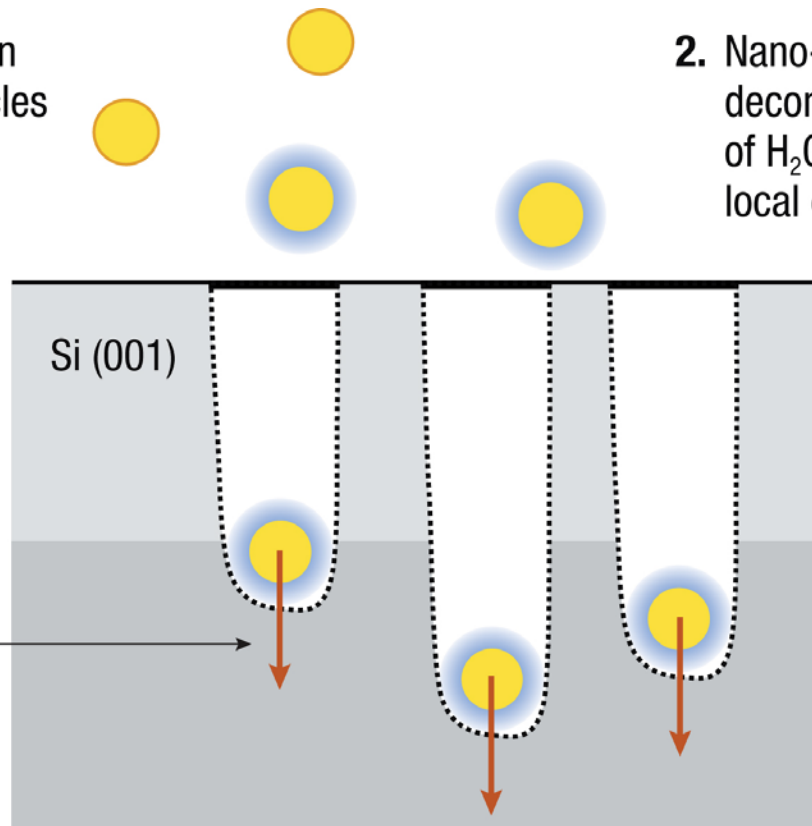
Mechanism: Nano-Pore Formation

Branz et al. APL, 2009

1. *In situ* production
of Au nanoparticles

2. Nano-catalytic
decomposition
of H_2O_2 to strong
local oxidant

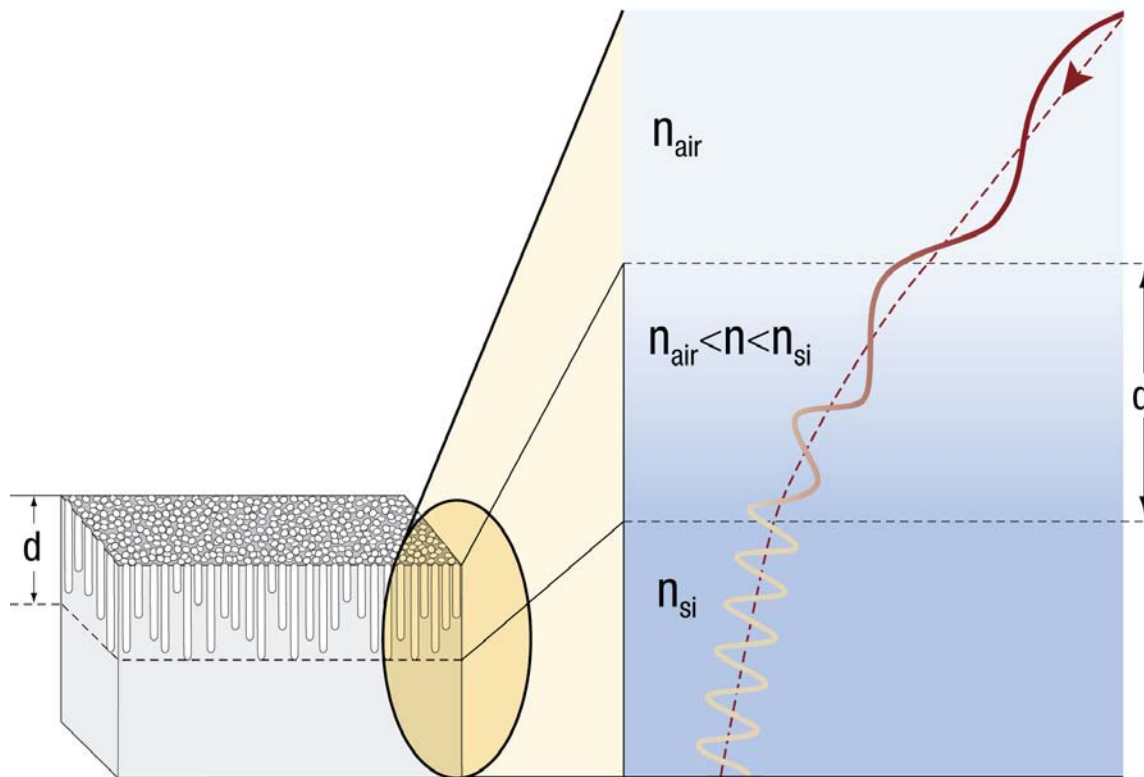
3. Local oxidation
of Si etching



4. Nanopores follow rapidly
etched direction

Branz et al. APL, 2009

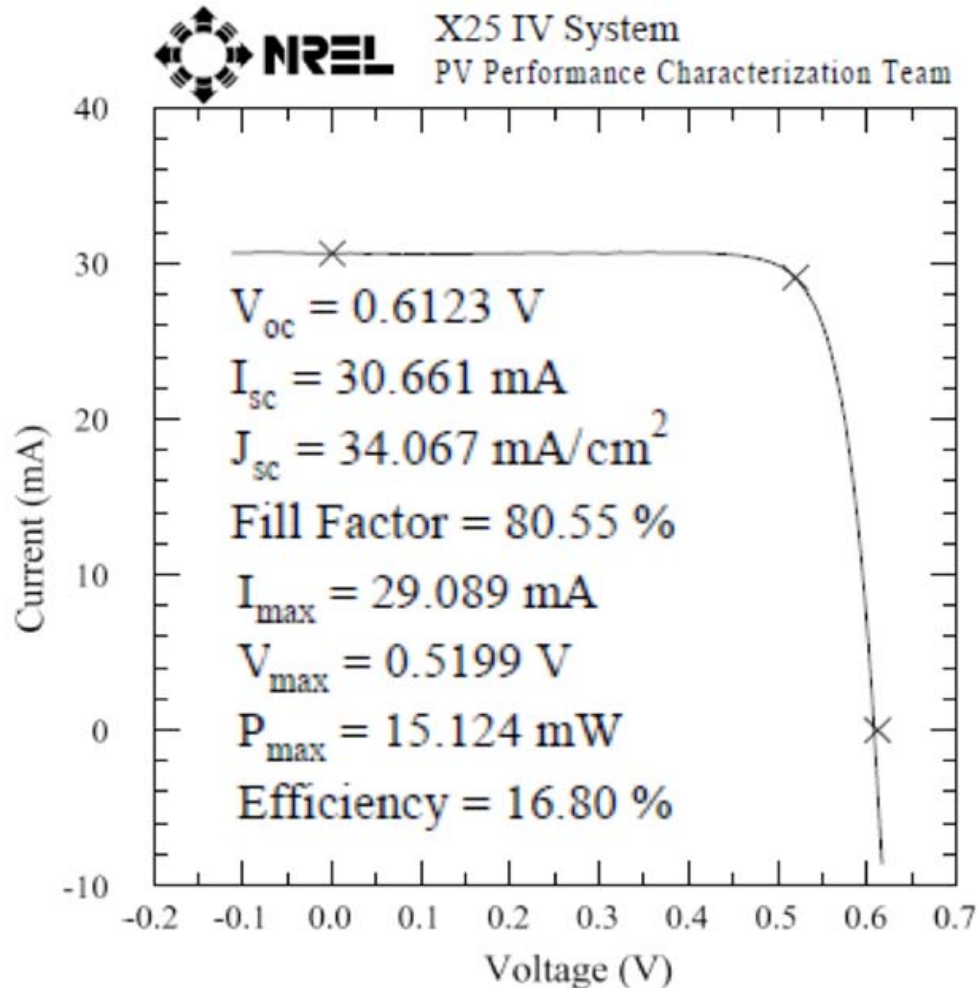
Black Silicon (graded-density)



- Nano-porous graded-density surface
- No abrupt interface between ambient and Si means no reflection
- Good AR at all angles since it does not rely on interference
- Graded-density depth “d” determines the AR range
 - AR needs $d > \lambda/2$

Background: Confirmed 16.8% Black Si Solar Cell

Yuan et al. APL, 2009

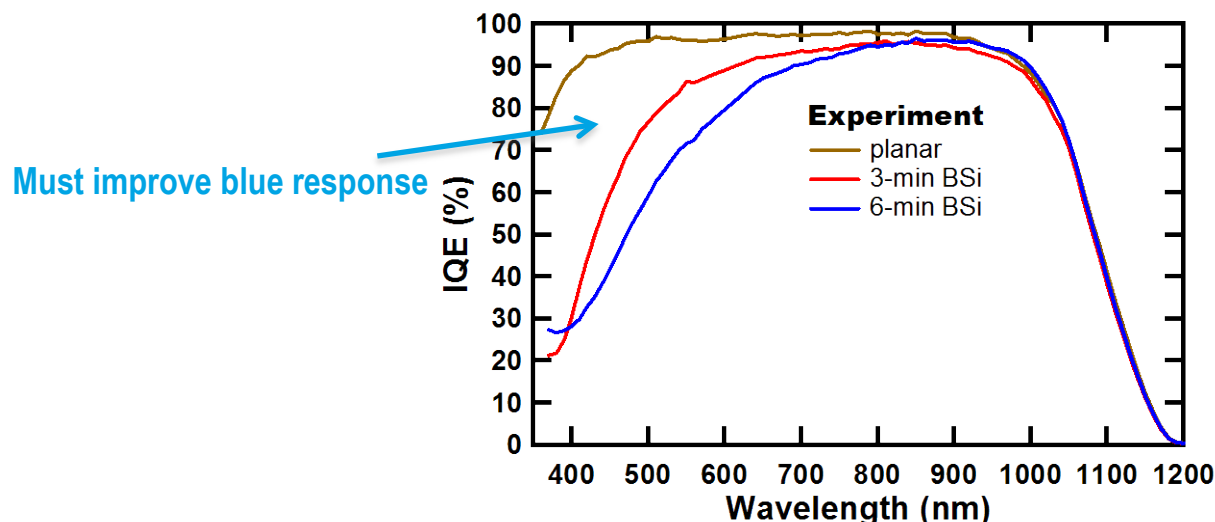


- One-step, 3-min, all liquid black Si etch
- No vacuum-based AR coating deposition
- Highest solar energy conversion efficiency reported with black Si AR
- Preliminary 14.9% on multi-crystalline Si

1. Improve black Si solar energy conversion efficiency to 17.8% and 15.8% on mono- and multi-crystalline Si, respectively
2. Apply one-step, all liquid black Si etch to at least four commercial multi-crystalline Si substrates
3. Evaluate angular performance and energy production of black Si solar cells
4. Demonstrate Au recycling method and develop industry-ready black Si etch processes

Approaches for Objective 1: Realize Full Efficiency Potential

- Reduce near-surface doping level to reduce Auger recombination within nano-porous region
- Improve surface passivation on the nano-porous surface
- Modify pore dimension to reduce surface area while keeping the excellent anti-reflection
- Improve backside scattering to increase light path length inside Si



Approaches for Objective 2: Apply Black Si on Multi-Crystalline Si

- Acquire industrial multi-crystalline Si substrates from at least four crystalline Si PV companies
- Perform and improve black Si etch process on multi-crystalline Si substrates
- Evaluate solar cells

Approaches for Objective 3: Evaluate Angular Performance

- Design rotatable stage for angular conversion efficiency measurement
- Measure angular dependent conversion efficiency on black Si solar cell and mini-module
- Estimate annual energy production improvement by use of annual diffuse and specular insolation data

Approaches for Objective 4: Industry-Ready Processes

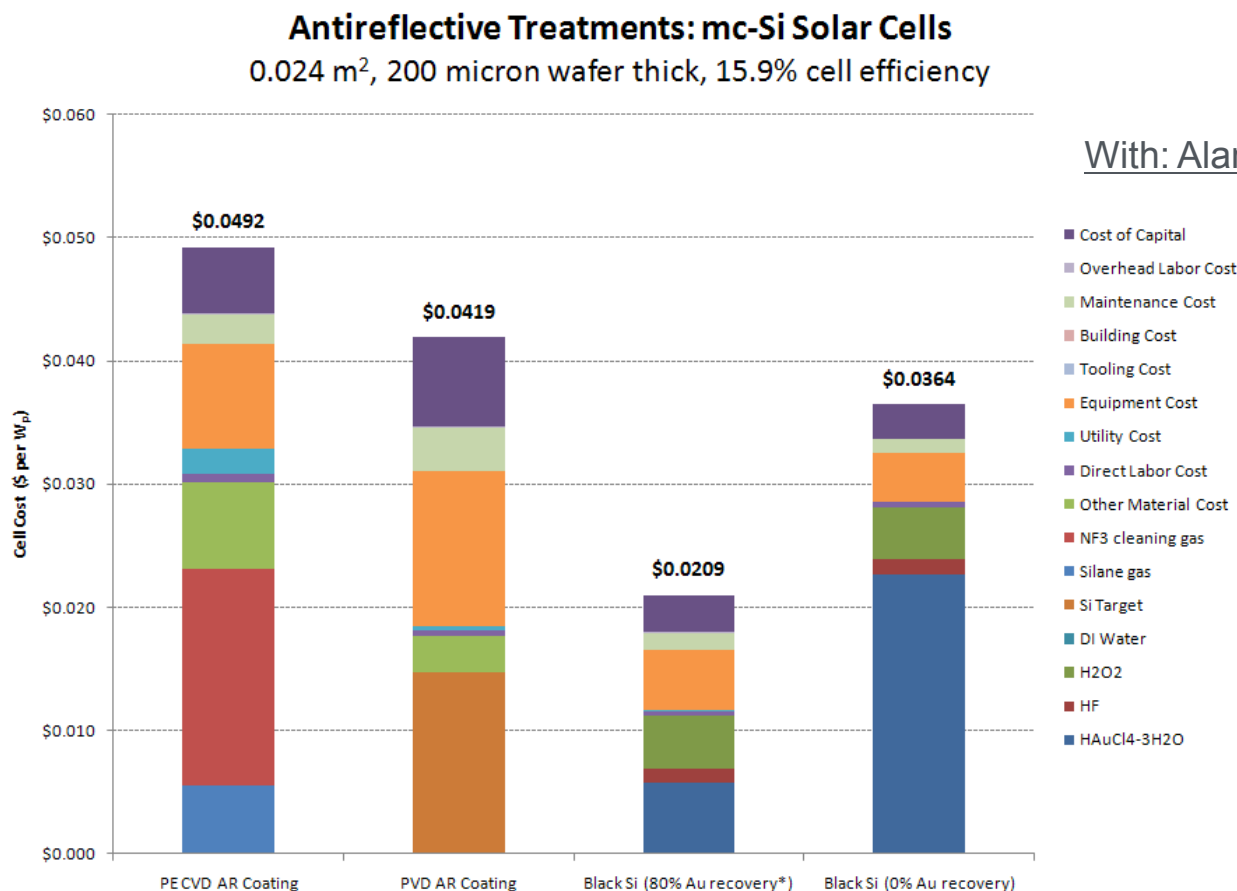
- Design and demonstrate Au recycling process
- Develop guidelines for design and operation of factory-scale black Si etch equipment

- Company A has provided both mono- and multi-crystalline Si substrates
- Company B and C have provided mono-crystalline Si substrates
- Company D and E have provided multi-crystalline Si substrates
- Company F has provided multi-crystalline Si ribbons
- Several companies are negotiating for licenses to the patents for the black Si technology

We have assembled an excellent project staff

- Dr. Howard Branz (Ph.D., MIT Physics) Principal Investigator
- Dr. Hao-Chih Yuan (Ph.D., University of Wisconsin Electrical Engineering), designed and fabricated first efficient black Si PV cells, Research Scientist
- Dr. Jihun Oh (Ph.D., MIT Materials Science) Post-doctoral Fellow
- Dr. Fatima Toor (Ph.D., Princeton University Electrical Engineering) Post-doctoral Fellow
- Vern Yost (M.S., Univ. Colorado Denver Chemistry);
- Matt Page (M.E. Colorado School of Mines Materials Engineering)

Accomplishments: Black Si Cost Analysis



- Assuming same conversion efficiency, black Si saves 2-3 cents/W compared to conventional AR
- 80% Au recycling is required for large cost advantage

Accomplishments: Black Si Cost & Environmental Impact Analysis In Progress

	Capex for 200-MW line	Power requirement (kWh/kW)	Equivalent CO ₂ (kg CO ₂ /kW)	GHG emission	Safety
Black Si AR	\$67.5M (no Au recovery) \$69.1M (80% Au recovery)	110	85	None	None
PECVD AR coating	\$75.5M	170	131	NF ₃ : 17,200x CO ₂ SF ₆ : 22,000x CO ₂	SiH ₄ : toxic, spontaneous flammable
PVD AR coating	\$81.2M	120	93		

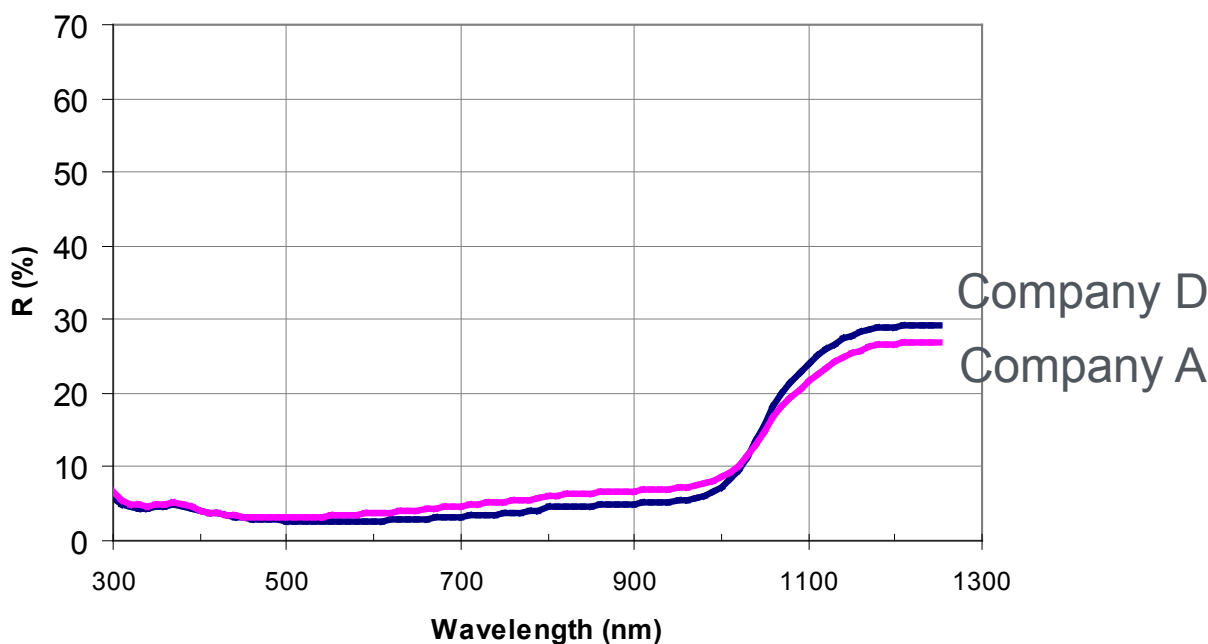
With : Alan Goodrich, NREL

Black Si AR:

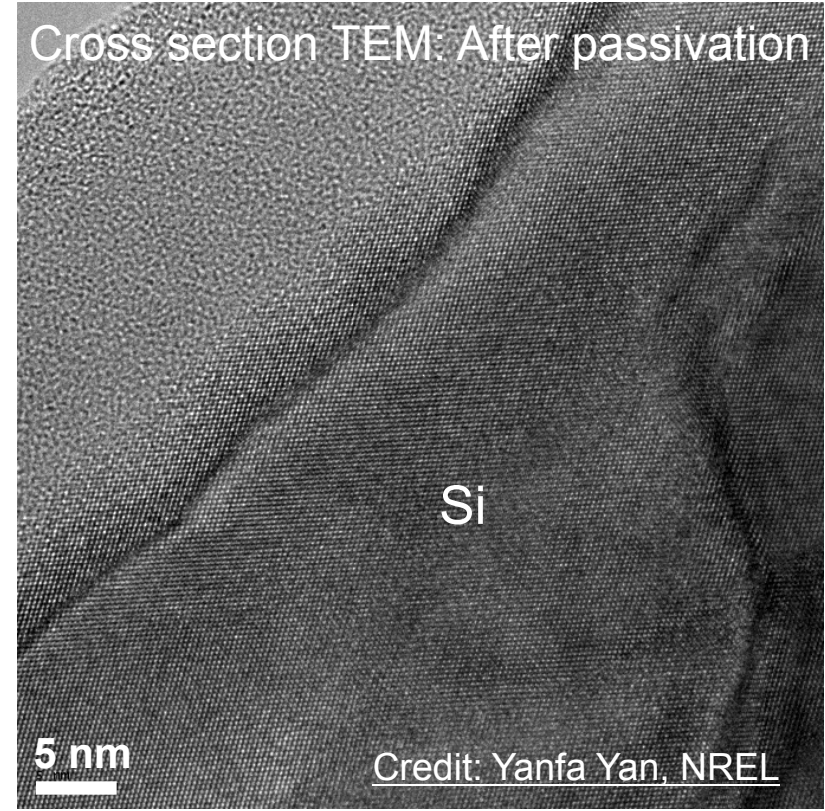
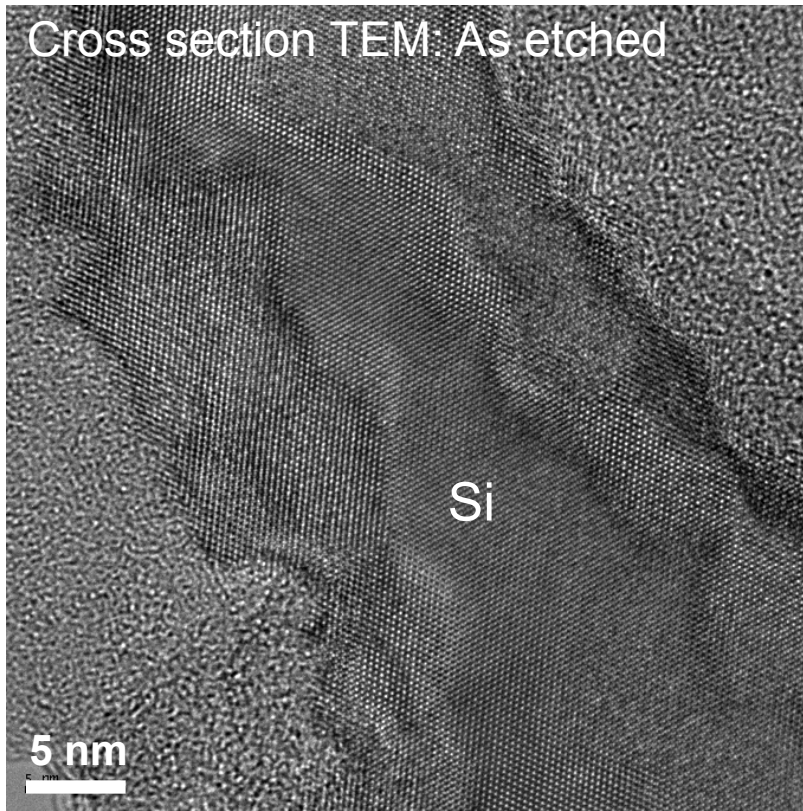
- cost effective
- requires less electricity
- emits no greenhouse gas
- safe

Accomplishments: Test Black Si on Industrial Multi-Crystalline Si

- We have acquired industrial multi-crystalline Si substrates from four crystalline Si PV companies
- We have achieved solar-spectrum-weighted (350-1000 nm) average reflectance of 4~6% on multi-crystalline black Si solar cells with 3-min black Si etch from two PV companies. Typical reflectance using conventional AR is > 7%.



Accomplishments: TEM of Black Si Surface Passivation



- Rough Si and Si-oxide interface resulted from black Si etch makes surface passivation challenging
- Our proprietary manufacturing-compatible passivation process smoothes the interface and improves passivation quality

- Experiments to determine which is dominant blue loss mechanism
 - Modify doping profile to reduce Auger recombination at near surface region
- Improve black Si etch throughput
- Optimize black Si etch on multi-crystalline Si substrates
- Modify pore dimension to reduce surface area

Upcoming key milestones

- | | |
|--|-----------|
| • Reduce near surface doping level to $\sim 10^{19} \text{ cm}^{-3}$ | Aug. 2010 |
| • Reduce black Si etch time to $< 30 \text{ sec}$ | Aug. 2010 |
| • Optimize black Si etch on multi-crystalline Si substrates | Oct. 2010 |
| • Increase pore feature size to $\sim 40 \text{ nm}$ | Dec. 2010 |

- NREL's one-step, all liquid black Si etch creates nanoporous graded-density surface that suppresses reflection over broad spectrum at normal and off-normal angles
- NREL's black Si AR is cheaper, more environmental friendly, and has potential for higher solar energy conversion efficiency than conventional AR techniques
- New surface passivation technique creates smooth interface and improves the passivation quality without increasing manufacturing cost
- Excellent team assembled to address key technical barriers to commercial adoption of black Si technology